Chapter 9

Chemical Hazards

Purpose:

This chapter states the policy and procedures to be followed in the procurement, transportation, storage, and use of hazardous chemicals at Hanford.

Scope:

This chapter will address the following topics:

- Application
- Responsibilities
- Information and Training
- Useful Life Planning
- Containers and Storage
- Transportation
- Use of Chemicals
- Pesticides
- Personal Protection
- Disposal
- Chemical Compatibility
- References
- Attachments

Application:

Every work place is exposed to hazards chemicals. Therefore, this chapter can be applied to every work place setting as follows.

Responsibilities:

It is the responsibility of supervision to know what chemicals are present, what hazards are associated, and what precautions are required. Supervision must then inform all personnel in the area of the hazards and enforce the necessary precautions.

Information and Training:

A hazardous chemical is a substance (liquid, solid, or gas) which may pose a risk. Chemicals can be hazardous for any one or more of the following reasons:

1. Toxicity, acute, or chronic
2. Mutual reactivity
3. Flammability
4. Pyrophoricity

5. Radioactivity, fissile reactivity
6. Irritation, Corrosivity
7. Decomposition, explosively or to form toxic products
8. Carcinogenicity, mutagenicity, and teratogenicity
9. Asphyxiation
10. Pathogenicity
11. High temperature/pressure
12. Age

Supervision shall ascertain the hazardous properties, alone and in combination, of each chemical present in the work environment. Adequate protection shall be determined and provided. Employees shall be taught the hazards of all chemicals present and the protective measures to be taken. Compliance with the designated procedures shall be enforced. Personnel training, chemical labeling, and Material Safety Data Sheets (MSDS) required by the OSHA Hazard Communication Standard must be complied with. See Attachments 1 and 2.

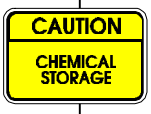
Useful Life Planning:

Before actions to acquire any chemical, supervision must identify any potential risk associated with that chemical and, as appropriate, plan and identify resources for:

1. Safe and proper transportation
2. Adequate facility design
3. Proper facility equipment and process design
4. Required protective equipment
5. Safe storage
6. Use and process procedures
7. Review of proposals and procedures
8. Employee training
9. Ultimate safe disposal

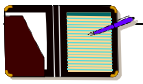
A MSDS shall be available for evaluation and assessment of the above items and retained in a location accessible to the work place. See Attachment 2.

If there is any question concerning the hazards of any chemical or the proper procedures or protective equipment, the responsible safety organization shall be consulted.



Containers and Storage:

1. Warehousing
   a) The local safety authority shall advise as to the maximum quantity of a hazardous chemical which should be stored at any location.



b) Bulk chemicals shall be stored in facilities specifically designed for the purpose. Personnel entry into confined spaces must be made according to the requirements.
c) Bins for bulk solids shall be equipped to assure safe removal and to prevent clogging. Personal entry to bins of tanks to assist in the gravity flow of solids shall be forbidden. Where bins have top openings, guard rails are required.
d) Chemical shall be segregated by type and reactivity. Adequate distance and/or wall separation shall be provided to prevent interaction. Buildings shall be designed to prevent, or be protected from, corrosivity or stored chemicals. Consideration shall be given to the hazards of storing certain chemicals on wooden pallets.
e) Ventilation in chemical storage areas shall follow guidelines of the ASHRAE criteria. Automatic fire detection and suppression shall be provided as required by the local safety authority. Potentially hazardous dusts shall be controlled.
f) Chemical storage space shall be kept clean and free from spillage. When spillage occurs the responsible operations personnel shall initiate the spill control and counter measures plan (SPCC) procedure with assistance from safety as necessary.
g) Chemicals shall not be stored near, or in the same enclosure with foodstuffs, including refrigeration appliances.
h) Proper personal protective equipment shall be made available in each chemical storage area.
i) Flammables shall be stored, transported, and handled according to applicable NFPA codes, and DOT Regulations.
j) The responsible safety organization shall be notified of all chemical purchases. The Hazard Communications Program should be utilized to control purchasing and warehouse functions for chemical, biological, and physical hazards.
k) Some chemicals will require issue in original containers or in approved containers or in approved containers specially designed to control the hazards of the chemicals.
l) All warning and instructions, in whatever form, supplied by the manufacturer of a chemical shall be followed implicitly unless more stringent requirements are imposed by the responsible safety organization. Warning labels shall not be removed or defaced. The employer shall ensure that each container in the work place is labeled, tagged, or marked in accordance with the requirements of the hazard communication standard.
m) Where freezing could damage materials or containers, protection against freezing shall be provided.
n) Certain items require protection from light and other forms of radiation.

o) Chemicals shall be marked or labeled with expiration date for those chemicals that may degrade or have a specified "shelf life."

2. Plant
   a) Where quantities of hazardous chemicals are stored in plant facilities, the storage requirements shall be the same as those in the primary warehouse. Standard Operating Procedures shall contain handling procedures where more stringent criteria is required.
   b) Access to plant stores of chemicals shall be restricted to designated, trained, and responsible employees.
   c) Laboratory and Shop
   d) The Quantities of chemicals kept in laboratories and shops shall be the minimum reasonable quantities. Long term storage of chemicals shall not be permitted in use areas. Chemicals shall be marked or labeled with expiration date for those chemicals that may degrade or have a specified "shelf life." Old or outdated chemicals shall be properly disposed of on a routine basis.
   e) Particular attention shall be paid to chemicals that may deteriorate to a more hazardous form with time. Storage conditions that may contribute to deterioration shall be avoided. These conditions may include freezing, high temperature, radiation, other chemical vapors, etc. Inventory listings shall be reviewed and updated periodically.
   f) As in warehousing, chemicals shall be segregated by type and compatibility and shall be provided with adequate barriers to prevent hazardous interaction.
   g) Chemicals shall be stored so that the possibilities of spillage or breakage are minimized.

Transportation:

1. Bulk

Tank cars and tank trucks shall be loaded, moved, and unloaded according to written procedures which comply with Department of Transportation (DOT) regulations and with recommendations of the Manufacturing Chemists Association.

2. Portable Containers
   a) Gas cylinders shall be constructed, inspected, labeled, and transported according to Subpart III K of this document.
   b) Carboys within a plant area shall be moved with proper carboy trucks.

c) Glass containers of hazardous liquids shall be moved in their original shipping containers, in rubber buckets, or in equivalent protective equipment. In any case, suitable precautions must be taken against breakage and/or spillage.
d) All containers of chemicals shall be compatible with the chemicals they contain. Improvised containers shall not be not used except with positive knowledge of the suitability by the user.
e) Containers may be stacked only so far as stability is assured. Adequate dunnage beneath and between tiers shall be used. The responsible safety organization shall be consulted for stacking evaluation and approval.

Use of Chemicals:

An important aspect of chemicals can be found in OSHA, 29 CFR 1910.119, "Process Safety Management of Highly Hazardous Chemicals." This section of OSHA contains requirements of preventing or minimizing the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. These releases may result in toxic, fire or explosive hazards.

Note: The use of <u>all</u> chemicals requires the worker to be knowledgeable of the hazards associated with their use. Workers must refer to the MSDS and other available material sources. Workers shall be properly trained on the hazards and use prior to any work with chemicals.

The scope of the OSHA requirements include;

- A process which involves a chemical at or above the specified threshold quantities listed in appendix A of the OSHA Standard under 29 CFR 1910.119 should be referred to for guidance.
- A process which involves a flammable liquid or gas (as defined in OSHA 29 CFR 1910.1200 (c) of this section) on site in one location in a quantity of 100.000 pounds (4535.9 kg) or more.
  Note: See OSHA for exceptions.

OSHA requires a "Process Hazard Analysis" to be performed by the employer. There shall be an initial process hazard analysis (hazard evaluation) on processes covered by this OSHA standard. The process hazard analysis shall be appropriate to the complexity of the process and shall identify, evaluate, and control the hazards involved in the process. Employers shall determine and document the priority order for conducting process hazard analysis based on a rationale which includes such considerations as extent of the process hazards, number of potentially affected employees, age of the process, and operating history of the process. The process hazard analysis shall be conducted as soon as possible, but not later than the schedule identified in this OSHA standard.

Refer to the OSHA Standard, 29 CFR 1910.119 and DOE requirements, including, DOE Order 5480.19, "Conduct of Operations" for details.

1. All process and shop uses of hazardous chemicals shall be by approved written procedures. Changes in chemicals or their use shall require approval equivalent to the original procedure.

2. Laboratory use of chemicals of high risk, such as the perchlorate and cyanide radicals, shall be used only with approved written procedures. Laboratory work which may involve hazardous reactions or conditions shall also be performed according to written procedures. Other laboratory operations will be performed with standard laboratory precautions.

3. Hazardous chemicals or operations which may generate or release hazardous gases, vapors, or dusts shall require adequate ventilation. In most cases, such work should be performed in hoods or glove boxes constructed and operated in accordance with the "ACGIH Industrial Ventilation Manual" and the "Nuclear Air Cleaning Handbook, ERDA 76-21."

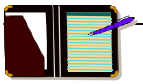
4. Process areas, shops, and laboratories using chemicals shall be kept clean and free from spillage. Auxiliary equipment such as pumps, blowers, ducts, protective gear, etc., shall be regularly inspected, tested, and maintained. Required hood face velocities shall be maintained.

5. Situations in which the risk of explosion is significant shall be evaluated and effective barriers (shields, distance, etc.), shall be imposed.

6. Special attention shall be given the procedures used with perchlorates. , ducts, blowers, etc., shall be designed to accommodate regular wash downs, and such wash downs shall be regularly performed. The Handbook of Laboratory Safety, published by the Chemical Rubber Co., is suggested as a reference on the safe handling of perchloric acid, perchlorates, and other hazardous chemicals. (See Chemical Compatibility, next section.)

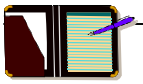
Chemical Compatibility

- Incompatible Chemicals
- Shock-Sensitive Chemicals
- Peroxides
- Suggested Segregation for Chemical Storage

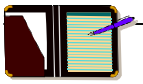


Some materials when mixed together can react violently and/or liberate toxic gas. Groups of materials that do so are termed incompatible. The classic example of materials that are incompatible are cyanides or sulfides and acid. Mixture of the two generate hydrogen cyanide or hydrogen sulfide, respectively, both very deadly gases. Laboratory staff must be aware of the groups of materials in their labs that could be incompatible. These materials bust be physically isolated from their incompatible counter parts (Works and Morrison 1995).

Chemical:	**Is incompatible with:**
Acetic acid	Chromic acid, nitric acid, hydroxyl compounds, ethylene glycol, perchloric acid, peroxides, permanganates
Acetylene	chlorine, bromine, copper, fluorine, silver, mercury
Acetone	Concentratednitric and sulfuric acid mixtures
Alkali and alkaline earth metals (such as powdered aluminum or magnesium, calcium,lithium, sodium, potassium)	Water, carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide, halogens
Ammonia (anhydrous)	Mercury (in manometers, for example), chlorine, calcium hypochlorite, idone, bromine, hydrofluoric acid (anhydrous)
Ammonium nitrate	acids, powdered metals, flammable liquids, chlorates, nitrites, sulfur, finely divided organic combustible materials
Aniline	nitric acid, hydrogen peroxide
Arsenical materials	any reducing agent
Azides	acids
Bromine	see chlorine
Calcium oxide	water
	calcium hypochlorite, all oxidizing agents
Carbon tetrachloride	sodium
Chlorates	Ammonium salts, acids, powdered metals, sulfur, finely divided organic or combustible materials
Chromic acid and chromium trioxide	acetic acid, napthalene, camphor, glycerol, alcohol, flammable liquids in general



Chlorine	Ammonia, acetyle, butadiene, butane, methane, propane (or other petroleum gases), hydrogen, sodium carbide, benzene, finely divided metals, turpentine
Chlorine dioxide	Ammonia, methane, phosphine, hydrogen sulfide
Copper	acetylene, hydrogen peroxide
Cumene hyroperoxide	acids (organic or inorganic)
Cyanides	acids
Flammable liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Fluorine	all other chemicals
Hydrocarbons (such as butane, propane, benzene)	fluorine, chlorine, bromine, chromic acid, sodium peroxide
Hydrocyanic acid	nitric acid, alkali
Hydrofluoric acid (anhydrous)	Ammonia (aqueous or anhydrous)
Hydrogen peroxide	Copper, chromium, iron, most metals or their salts, alcohols, acetone, organic materials, aniline, nitromethane, combustible materials
Hydrogen sulfide	Fuming nitric acid, oxidizing gases
Hypochlorites	acids, activated carbon
Iodine	acetylen, ammonia (aqueous or anhydrous)
Mercury	Acetylene, fulminic acid, ammonia
Nitrates	sulfuric acid
Nitric acid (concentrated	Acetic acid, aniline, chromic acid, hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases, copper, brass any heavy metals
Nitrities	acids
Nitroparaffins	inorganic bases, amines
Oxalic acid	silver, mercury
Oxygen	oils, grease, hydrogen: flammable liquids, solids, or gases
Percholoric acid	acetic anhydride, bismuth and its alloys, alcohol, paper, wood, grease, oils
Peroxides, organic	Acids (organic or mineral), avoid friction, store cold
Phosporus (white)	Air, oxygen, alkali, reducing agents



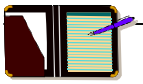
Potassium	carbon tetrachloride, carbon dioxide, water
Potassium chlorate	sulfuic and other acids
Potassium perchlorate (see also chlorates)	sulfuic and other acids
Potassium permanganate	Glycerol, ethylene glycol, benzaldehyde, sulfuric acid
Selenides	reducing agents
Silver	Acetylene, oxalic acid, tartartic acid, ammonium compounds, fulminic acid
Sodium	carbon tetrachloride, carbon dioxide, water
Sodium nitrite	Ammonium nitrate and other ammonium salts
Sodium peroxide	ethyl or methyl alcohol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, glycerin, ethylene glycol, ethyl acetate, methyl acetate, furfural
Sulfides	acids
Sulfuric acid	Potassium chlorate, potassium perchlorate, potassium permanganate (similar compounds of light metals, such as sodium, lithium)
Tellurides	reducing agents

From *Safety in Academic Chemistry Laboratories*, Sixth Edition. 1995. Committee on Chemical Safety, American Chemical Society, Washington, DC.

Shock-Sensitive Chemicals:

These chemicals require special handling techniques and conditions. This list of shock-sensitive chemicals is not all-inclusive. Review the material safety data sheet for reactivity information concerning the chemicals you use. Please contact the Hazardous Materials Environmental Compliance Representative for instructions and assistance if any of these chemicals are purchased or created in the laboratory.

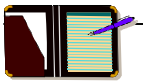
acetylides of heavy metals
aluminum ophorite explosive
amatol
ammonal
ammonium Perchlorate
ammonium picrate
ammonium salt lattice
2,2-azonaphthalene
azoxybenzene
butyl tetryl
copper acetylide
cyanuric triazide
cyclotrimethylenetrinitramine



cyclotetramethylene tranitramine
diazomethane
dimethyl amino azobenzene-2-naphthalene
2,3-dimethyl azobenzene
dinitroglycerine
dinitrophenol
dinitrophenolates
dinitrophenyl hydrazine
dipicryl sulfone
dipicylamine
erythritol tetranitrates
explosive mixtures
fulminate of silver
fulminating gold
fulminating mercury
fulminating platinum
germane
guanyl nitrosamino guanyltetrazene
guanyl nitrosamino auanylidene
hydrazine
guanylidene
hexite
hexanitrodiphenylamine
hexanitrostilbene
hexogen
hydrazoic acid
lead azide
lead mannite
lead mononitroresorcinate
lead salts
lead styphnate
magnesium ophorite
mannitol hexanitrate
mercury tartrate
3-methyl-4-dimethylaminoazobenzene
mononitrotoluene
nitroaminotetrozole
nitrated carbohydrate
nitrated polyhydric alcohol
nitrocellulose
nitrogen trichloride
nitrogen tri-iodide
nitroglycerin
nitroglycol
nitrogauanidine
nitroparaffins
nitronium perchlorate
organic amine nitrates
organic nitramines
organic peroxides
perchloric acid
perchlorate salts
peroxide formers
1-phenylazo-2-naphthol
picramic acid
picrate salts
picratol
picric acid
picryl chloride
picryl fluoride
polynitroaromatics
potassium nitroaminotetrazole
silver acetylide
silver azide
silver styphnate
sodatol
sodium amatol
sodium azide
sodium dinitro-ortho-cresolate
sodium nitrate-potassium explosive mixtures
syphinic acid
tetrazene
tetranitrocarbazole
tetrytol
trinitroanisole
trinitrobenzene
trinitrobenzoic acid
trinitrocresol
trinitronaphthalene
trinitrophenetol
trinitrophloro-glucinol
trinitrotoluene
tritonal
urea nitrate

Peroxides:

Organic peroxides are among the most hazardous substances handled in the chemical laboratory. They are generally low-power explosives that are sensitive to shock, sparks, or other accidental ignition. They are far more shock-sensitive than most primary explosives, such as TNT.



Also potentially hazardous are compounds that undergo auto-oxidation to form organic hydroperoxides and/or peroxides when exposed to the oxygen in air. Especially dangerous are ether bottles that have evaporated to dryness. A peroxide present as a contaminant in a reagent or solvent can be very hazardous and change the course of a planned reaction (National Research Council I 98 1).

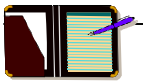
Because they have a limited shelf life, ethers should be bought in the smallest practicable containers appropriate to the rate of usage within the facility, preferably in 500-mL containers or less. Small containers also eliminate much of the need for frequent checking of the conditions of the contents of a large container. No matter what size container is purchased, each container should be dated when it is received and placed in stock. For isopropyl and diethyl ethers, it is recommended that even unopened containers be disposed of after 1 year, while opened containers should be discarded 6 months after they are first used, if they have not been tested periodically during the interval. Opened containers should be tested after 1 month and continue to be tested until emptied, or at frequent intervals (Steere 1971).

Types of Compounds Known to Auto-oxidize to Form Peroxides
Aldehydes
Ethers, especially cyclic ethers and those containing primary and secondary alkyl groups (never distill an ether before it has been shown to be free of peroxide)
Compounds containing benzylic hydrogens
Compounds containing allylic hydrogens (C=C-CH), including most alkenes; vinyl and vinylidene compounds
Compounds containing a tertiary C-H group (e.g., decalin and 2,5-dimethylhexane)

Classes of Chemicals That Can Form Peroxides Upon Aging:

Class I: Unsaturated materials, especially those of low molecular weight, may polymerize violently and hazardously due to peroxide initiation.

Acrylic acid	Tetrafluroethylene
Acrylonitrile	Vinyl acetate
Butadiene	Vinyl acetylene
Chlorobutadiene (chloroprene)	Vinyl chloride
Chlorotrifluoroethylene	Vinyl pyridine
Methyl methacrylate	Vinylidene chloride
Styrene	



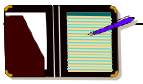
Class 11: The following chemicals are a peroxide hazard upon concentration (distillation/evaporation). A test for peroxide should be performed if concentration is intended or suspected.

Acetal	Dioxane (*p*-dioxane)
Cumene	Ethylene Glycol dimethyl ether (glyme)
Cyclohexene	Foran
Cyclooctene	Methyl acetylene
Cyclopentene	Methyl cyclopentane
Diacetylene	Methyl-*i*-butyl ketone
Dicyclopentadiene	Tetrahydrofuran
Diethylene glycol dimethyl ether (diglyme)	Tetrahydronaphthalene
Diethyl ether	Vinyl ethers

Class III: Peroxides derived from the following compounds may explode without concentration.

Organic	Inorganic
Divinyl ether	Potassium metal
Divinyl acetylene	Potassium amide
Isopropyl ether	Sodium amide (sodamide)
Vinylidene chloride	

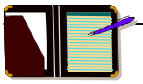
NOTE: Lists are illustrative but not exhaustive.



Suggested Segregation for Chemical Storage:

FLAMMABLES • Store in grounded flammable liquid-storage cabinets • Separate from oxidizing materials *examples* acetone ethanol glacial acetic acid	NON-FLAMMABLE SOLVENTS • Store in cabinet • Can be stored with flammable liquids • Separate from oxidizing materials *Examples* carbon tetrachloride ethylene glycol mineral oil	ACIDS • Store in cabinet of non-combustible material • Separate oxidizing acids from organic acids • Separate from caustics, cyanides, sulfides *examples* nitric acid hydrochloric acid sulfuric acid
CAUSTICS • Store in dry area • Separate from acids *examples* ammonium hydroxide sodium hydroxide potassium hydroxide	WATER-REACTIVE CHEMICALS • Store in cool, dry location • Separate from aqueous solutions Protect from fire-sprinkler water *Examples* sodium potassium lithium	OXIDIZERS • Store in cabinet of non-combustible material • Separate from flammable and combustible materials *examples* sodium hypochlorite benzoyl peroxide potassium permanganate
NON-OXIDIZING COMPRESSED GASES • Store in well-ventilated area • Separate physically from oxidizing compressed gases *examples* nitrogen hydrogen carbon dioxide	OXIDIZING COMPRESSED GASES • Separate physically from flammable compressed gases *Examples* oxygen chlorine nitrous oxide	NON-VOLATILE, NON- REACTIVE SOLIDS • Store in cabinets or open shelves with edge guards *examples* agar sodium chloride sodium bicarbonate

McGill University, Montreal, Quebec.



Chemical Compatibility References:

Committee on Chemical Safety. 1995. *Safety in Academic Chemistry Laboratories,* Sixth Edition. American Chemical Society, Washington, DC.

National Research Council. 1981. *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals.* Washington, DC.

Works, R and J Morrison. 1995. *Chemical Hygiene Plan for Chemistry Laboratories.* Illinois State University Office of Environmental Health and Safety, Normal, IL.

Steere, NV (ed). 1971. "Control of peroxides in Ethers," in *CRC Handbook of Laboratory Safety,* Second Edition. CRC Press, Boca Raton, FL.

Pesticides:

1. Only pesticides formally approved by DOE-RL and the State of Washington may be purchased, stored, or used. Each contractor shall annually propose to RL the pesticides to be used in the following calendar year.

2. "Restricted Use" Pesticides must be approved by RL-ESH before use at RL facilities, and then only after exhaustive evaluation reveals an emergency condition or no acceptable substitute exists. "Restricted Use" pesticides shall be administered only by a licensed commercial applicator.

3. Pesticides may be used or applied only by persons certified in their use by the Department of Agriculture, or by persons under the direct cognizance of a person so certified.

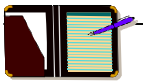
4. Commercial applicators contracted for services at the Hanford Site must have proper and valid State of Washington Licensing and comply with Hanford Procedures.

Personnel Protection:

Personnel working with hazardous chemicals shall be provided with, and required to use, the appropriate protective devices.

Disposal:

1. Supervisors in charge of work places storing and/or using chemicals shall routinely inventory such chemicals for the purpose of



eliminating those which are no longer used, those which are excess to needs, and those which may have deteriorated.

2. Chemicals identified in a., immediately above, shall disposed of by the supervisor according to procedures approved by the responsible safety authority. The method of disposal shall be determined by the economic value, the risks to humans and the environment, the availability of disposal facilities, and the requirements of applicable regulations.

References:

- 29 CFR 1910, Subpart H, “Hazardous Materials”
- 29 CFR 1910, Subpart I, “Personal Protective Equipment.”
- 29 CFR 1910, Subpart Z, “Toxic and Hazardous Substances.”
- 29 CFR 1910.119, "Process Safety Management of Highly Hazardous Chemicals."
- 29 CFR 1910.1200. “Hazard Communication Standard.”
- 40 CFR Parts 162 through 171, “Regulations for the Enforcement of the Federal Insecticide, Fungicide, and Rodenticide Act.”
- DOE Order 5480.19, "Conduct of Operations"
- NFPA 49 and 491 M, “Hazardous Chemicals Data” and “Manual of Hazardous Chemical Reactions.
- ASHRAE Standards.

Attachments:

- Attachment 1: *Hazardous Chemicals Training Records*
- Attachment 2: *Material Safety Data Sheets(MSDS) Storage Location*

Attachment 1:

Hazardous Chemicals Training Records

Please insert a copy of applicable records following this page or indicate the location of these records on the form below.

Facility Name:		
Training Records Location:	**Initial:**	**Date:**

Attachment 2:

Material Safety Data Sheets (MSDS) Storage Location

Please insert a copy of applicable records following this page or indicate the location of these records on the form below.

Facility Name:		
MSDS's Location:	**Initial:**	**Date:**